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Structural Investigations of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ glass-ceramics by Solid State NMR

S V Pershina[1], M Y Dzuba[1,2], S G Vlasova[2], Y V Baklanova[3]

[1]Institute of High-Temperature Electrochemistry, Ural Branch of the Russian Academy of Sciences, 620137, Akademicheskaya st., 20, Yekaterinburg, Russian Federation

[2]Ural Federal University named after the first President of Russia B.N. Yeltsin, 620002, Mira st., 19, Yekaterinburg, Russian Federation

[3] Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620990, Pervomayskaya st., 91, Yekaterinburg, Russian Federation

E-mail: Svpershina_86@mail.ru

Abstract. NASICON-type conductors based on $LiGe_2(PO_4)_3$ are very promising lithium-conducting electrolytes for all-solid-state lithium-ion and lithium batteries. Al-doped $LiGe_2(PO_4)_3$ solid electrolytes possessed higher conductivity (~10^{-4} S/cm at room temperature) and stability versus metallic Li. In this paper, we present the structure study of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ compound. Fast lithium-ion conductor $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ solid electrolyte have been obtained through glass crystallization at 820 °C during 8 h. Structural positions occupied by atoms have been examined by solid state nuclear magnetic resonance experiments. ^6Li, ^7Li, ^{27}Al и ^{31}P NMR measurements have been performed at room temperature.

1. Introduction

All-solid-state lithium batteries using a solid electrolyte have long-life, safety, excellent rate capability, as well as high voltage and capacity, so they are considered as next-generation power sources [1-3]. Solid state lithium ion conductors for these applications must be resistant to the aggressive Li, have high lithium ion conductivity at room temperature (> 10^{-4} S cm^{-1}) and thermal stability, and also dense microstructure [4]. In particular, solid electrolytes with NASICON (Na Super Ionic CONductor) structure and formula $LiM_2(PO_4)_3$ (M^{IV}= Ge, Ti, Sn, and Hf) have been extensively studied [1-4]. It is known that the conductivity increases by 3-4 orders of magnitude at room temperature when $Ge^{4+}(Ti^{4+})$ is partially replaced by Al^{3+}, Y^{3+} or Sc^{3+} ions [1, 5, 6]. In particular, $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ system attracts a lot of interest due to its high conductivity and stability against metallic Li [2, 5]. Among Al-doped $LiGe_2(PO_4)_3$ solid electrolytes, $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ composition (or LAGP) exhibits the highest conductivity [6, 7], however, the conductivity of this electrolyte is considerably dependent on the synthesis conditions. It should be noted that crystallization of a glass corresponding to the formula $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ is the most viable method of obtaining a high-conductivity LAGP electrolyte compared to conventional solid-state and sol-gel methods [6-8].

The framework of NASICON-type materials can be described as a covalent skeleton $M_2(PO_4)_3$ with corner-sharing MO_6 octahedra and PO_4 tetrahedra which form a three-dimensional (3D) network [1, 4, 5]. In this case, two MO_6 octahedra and three PO_4 tetrahedrons share oxygen atoms. In NASICON-type structure there are two possible crystallographic sites for Li ions migration: octahedral (Li_1) and 10-fold

coordinated (Li_2). Li_1 positions should be fully occupied and Li_2 positions should all be vacant to provide a high conductivity of the electrolyte. The tetrahedral positions in the NASICON structure should be completely occupied by P^{5+} ions, and Al^{3+} cations are only in octahedral sites. The presence of Al^{3+} ions in tetrahedral coordination indicates the presence of phosphate-based impurities even in very small quantities, which negative influence on ionic conductivity. Determining the coordination of Al^{3+} ions in NASICON-type materials is useful for clarifying the phase composition of samples. The structure of the LAGP ceramic electrolytes has been the subject of a large number of works [9-11], however, only a few studies on LAGP glass-ceramics have been performed [3, 12]. For this reason, we focused on the structural aspects of this type of compound using nuclear magnetic resonance (NMR) experiments with magic-angle spinning (MAS) at room temperature.

2. Experimental

$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ glass-ceramics were obtained by glass crystallization. The starting glass of $19.75Li_2O$–$6.17Al_2O_3$–$37.04GeO_2$–$37.04P_2O_5$ composition for obtaining $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ glass-ceramics was synthesized by melt quenching. During the synthesis of glass and glass-ceramics at high temperatures, part of Li_2O can volatilize; therefore, Li was taken in excess.

Li_2CO_3 (>99.4%), Al_2O_3 (>99.9%), GeO_2 (>99.9%) and $NH_4H_2PO_4$ (≥98.0%) served as precursors for obtaining glass. Aluminium and germanium oxides were previously heated at 1000 °C for 1 h, and Li_2CO_3 was dried at 300 °C for 3 h. The starting components were thoroughly mixed together. The mix was heated stepwise up to 500 °C to remove volatile components. The resulting mixture was then melted in a Pt crucible at 1450 °C for 1 h. The melt was quenched between preheated steel plates. The procedure yielded transparent colorless parallel-sided plates without any impurities. The samples were annealed at 500 °C during 0.5 h to relieve thermal stresses, then polished on both sides and crystallized at 820 °C for 8 h at the rate of 3 °C min⁻¹. After crystallization, the samples were slowly cooled down to room temperature in the furnace. In appearance the samples were white.

The amorphous structure of the original glass and the phase composition of the obtained glass-ceramics were determined by X-ray diffraction method (XRD) with a Rigaku D/MAX-2200VL/PC diffractometer (Rigaku, Japan) over a 2θ range of 10–60° at room temperature. The collected data were processed with the FULLPROF program.

The ^6Li, ^7Li, ^{27}Al и ^{31}P MAS NMR spectra were obtained by using Agilent 400WB spectrometer (B_0 = 9.4 T, ^6Li, ^7Li, ^{27}Al and ^{31}P Larmor frequencies are 58.87, 155.46, 104.31 и 161.94 MHz, respectively) with standart Agilent 4.0 mm MAS Probe head at room temperature at MAS speed of 5–10 kHz. A 9.7 M LiCl, 1.1M $Al(NO_3)_3$ and H_3PO_4 were used as a references. The spectra deconvolution was performed with thy DMFit program [13].

3. Result and discussion

The X-ray powder diffraction patterns of glass-ceramic electrolytes are shown in Figure 1. According to the XRD analysis, the pattern reflections of the obtained electrolytes corresponded to the $LiGe_2(PO_4)_3$ phase, which is indexed as a hexagonal structure with the space group *R-3c* (#167), and also the GeO_2 impurity phase, Figure 1. *R-3c* space group is typical for NASICON-type structure [2, 6]. It is known that a partial substitution of Ge^{4+} ions (r_i = 0,53 Å) for Al^{3+} ions (r_i = 0,535 Å) with almost similar ionic radii yields solid solutions $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ at $0.1 \leq x \leq 0.6$ [6, 7].

The ^{27}Al MAS NMR spectrum of LAGP glass-ceramics shows the narrow single line with a maximum at δ = 14.8 ppm (Figure 2), which can be unambiguously attributed to Al^{3+} ions in an octahedral positions since Al takes the place of Ge in LAGP framework. Indeed, in the ^{27}Al NMR spectra of the $Li_{1+x}Al_xM_{2-x}(PO_4)_3$ (M = Ti, Ge; x = 0.0–0.5) compositions, the most intensive spectral component at δ = 14 ppm corresponds to AlO_6, while the line at ~ 41 ppm assigned to tetrahedrally coordinated aluminum [10]. The presence of this line in the NMR spectrum indicates the appearance of the $AlPO_4$ impurity phase in the compounds; moreover, the intensity of this line usually growths with increasing dopant concentration [14]. However, unlike the above-mentioned compounds, the presence of the single signal in the ^{27}Al NMR spectrum for the studied LAGP glass-ceramic samples is in

complete agreement with the NASICON-type structure. The absence of the signal from the $AlPO_4$ impurity phase indicates wide stability interval of $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ solid solutions.

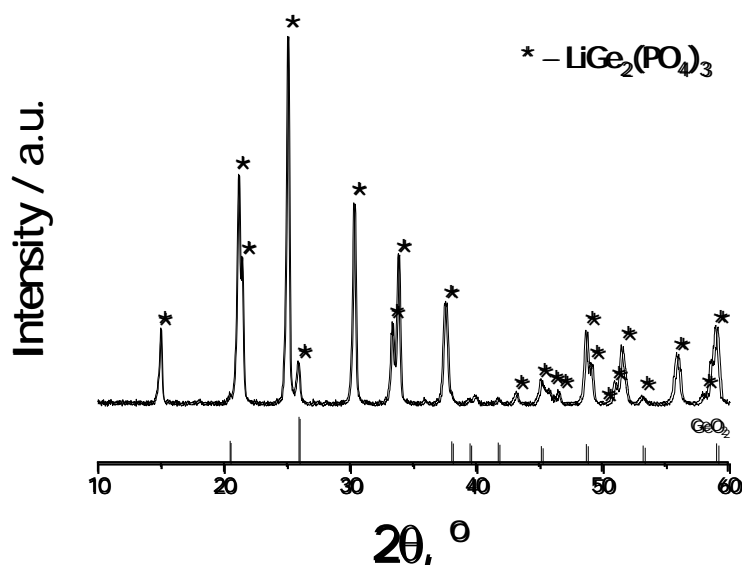**Figure 1.** XRD pattern at room temperature of the $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ glass-ceramics crystallized at 820 °C, and line diagram for GeO_2.
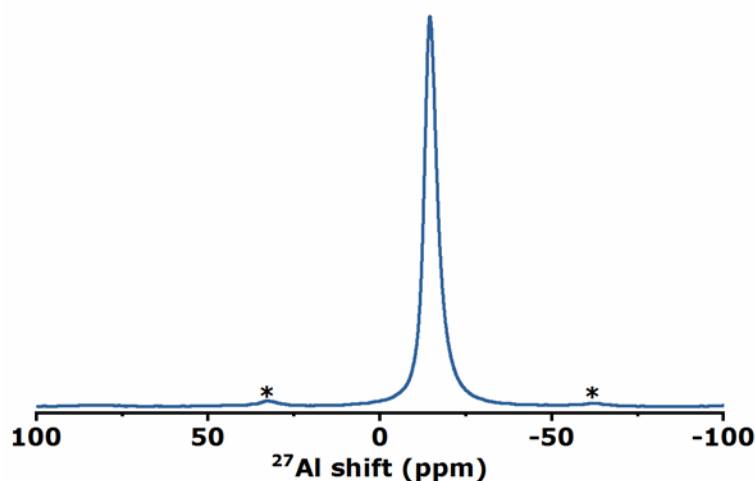

Figure 2. The ^{27}Al MAS NMR spectrum of LAGP glass-ceramics crystallized at 820 °C. The spinning sidebands are marked with asterisks.

The ^{31}P MAS NMR spectrum of LAGP glass-ceramics represents a superposition of six asymmetric lines with different chemical shift values, indicating six different environments of P^{5+} ions, Figure 3. The line shape modelling of the NMR spectrum allowed to distinguish four components with different PO_4^{3-} environments in the LAGP crystal structure. So, the most intensive lines with maxima at $\delta \sim -42$ ppm and $\delta \sim 37$ ppm should be attributed to $P(OGe)_4$ and $P(OGe)_3(OAl)_1$ groups, respectively. While less intensive lines with more positive chemical shift values at $\delta \sim -32$ ppm and $\delta \sim -28$ ppm can be assigned to $P(OGe)_2(OAl)_2$ and $P(OGe)_1(OAl)_3$ groups, respectively. The $P(OGe)_4/ P(OGe)_3(OAl)_1/ P(OGe)_2(OAl)_2/ P(OGe)_1(OAl)_3$ components ratio is equal 24 / 54 / 16 / 6 (in %). Two lines with low

intensity at $\delta \sim$ -4 ppm and $\delta \sim$ -7 ppm are observed in the range of 25 to 50 ppm additionally to the main lines; they can be attributed to NMR signals from possible Li_3PO_4 and/or $Li_4P_2O_7$ impurity phases [12]. These impurities have not been identified by XRD analysis, possibly due to their low content.
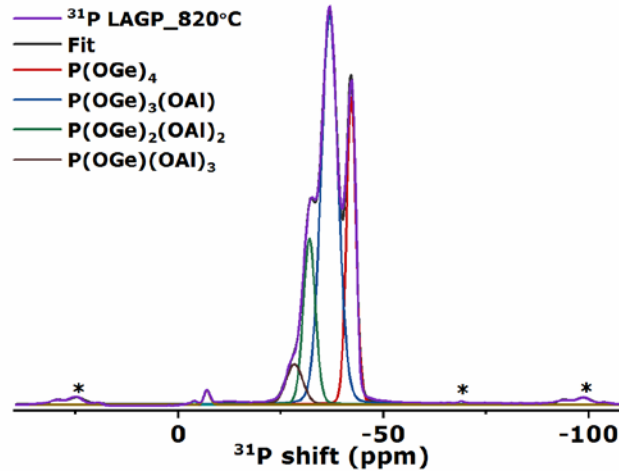

Figure 3. The ^{31}P MAS NMR spectrum at room temperature of LAGP glass-ceramics samples crystallized at 820 °C (purple line). The computer modeling results (Gaussian / Lorentzian model) of the spectrum shape with lines corresponding to nonequivalent phosphate groups are presented by black curve. The spinning sidebands are marked with asterisks.

The $^{6,7}Li$ MAS NMR spectra of LAGP glass-ceramics are represented by a narrow single line with the maximum positions at δ = -0.5 ppm, respectively, Figures 4 and 5. According to the LAGP crystal structure, Li^+ ions occupy at least two different positions which are in close near and form the three-dimensional channel for lithium-ion migration. However, it is not possible to separate these positions even on the ^6Li MAS NMR spectra at room temperature due to the high ion exchange between them.
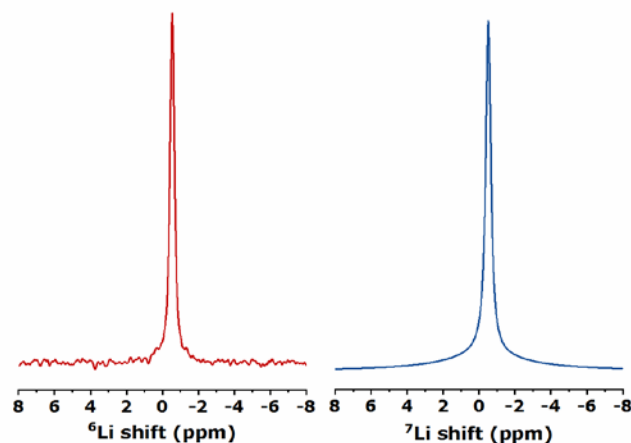

Figure 4. ^6Li (left) and ^7Li (right) MAS NMR spectra of LAGP glass-ceramics samples crystallized at 820 °C.

4. Conclusions

In this work the structure of promising $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ glass-ceramic electrolytes crystallized at 820 °C were studied using NMR method.

The assignment of the ^{31}P and ^{27}Al MAS NMR lines to various phosphate and aluminate structural groups was performed.

It was established that all Al^{3+} ions are in the octahedral environment, which is typical for the NASICON-type structure.

It was confirmed that no $AlPO_4$ impurity was presented in the studied samples.

Acknowledgement

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